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**Stratospheric Tracers of Atmospheric Transport  
(STRAT) Campaign: ER-2 Participation**

**Final Technical Report**

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## A Final Report: STRAT Campaign: ER-2 Participation (NASA Cooperative Agreement NCC 2-892)

The NASA Stratospheric Tracers of Atmospheric Transport (STRAT) mission was initiated to advance knowledge of the major transport mechanisms of the upper troposphere-lower stratosphere. This is the region of the atmosphere within which exchange processes take place that critically determine the response of the climate system and ozone distribution to changing conditions triggered by the release of chemicals at the surface. The mission series that extended from October 1995 to November 1997 was extremely successful. The scientific advances that emerged from that mission include analyses of:

- troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_3$ ;
- the effects of tropical cirrus clouds on the abundance of lower stratospheric ozone;
- the role of  $\text{HO}_x$  in super- and subsonic aircraft exhaust plumes; and
- dehydration and denitrification in the arctic polar vortex during the 1995–96 winter.

The abstracts from published results of this mission are presented here in the order that they appeared in the literature.

1. Dessler, A. E., K. Minschwaner, E. M. Weinstock, E. J. Hints, and J. G. Anderson, "The effects of tropical cirrus clouds on the abundance of lower stratospheric ozone," *J. Atmos. Chem.* **23**, 209–220, 1996. The distribution of many chemical constituents of the atmosphere (e.g., ozone) is at least partially determined by the distribution of net radiative heating in the atmosphere. In this paper, we demonstrate the significant effect of high cirrus clouds on the net radiative heating of the tropical lower stratosphere. A model of tropical lower stratospheric ozone is then used to demonstrate the sensitivity of calculated ozone to the varying cloud cover used in the model. We conclude that calculated ozone is sensitive to the inclusion of clouds in models and that models of the atmosphere should include a realistic description of the tropical cirrus clouds in order to accurately simulate the chemical composition of the atmosphere.
2. Hanisco, T. F., P. O. Wennberg, R. C. Cohen, J. G. Anderson, D. W. Fahey, E. R. Keim, R. S. Gao, R. C. Wamsley, S. G. Donnelly, L. A. Del Negro, R. J. Salawitch, K. K. Kelly, and M. H. Proffitt, "The role of  $\text{HO}_x$  in super- and subsonic aircraft exhaust plumes," *Geophys. Res. Lett.* **24**, 65–68, 1997. The generation of sulfuric acid aerosols in aircraft exhaust has emerged as a critical issue in determining the impact of supersonic aircraft on stratospheric ozone. It has long been held that the first step in the mechanism of aerosol formation is the oxidation of  $\text{SO}_2$  emitted from the engine by OH in the exhaust plume. We report here *in situ* measurements of OH and  $\text{HO}_2$  in the exhaust plumes of a supersonic (Air France Concorde) and a subsonic (NASA ER-2) aircraft in the lower stratosphere. These measurements imply that reactions with OH are responsible for oxidizing only a small fraction of  $\text{SO}_2$  (2%), and thus cannot explain the large number of particles observed in the exhaust wake of the Concorde.
3. Wennberg, P. O., T. F. Hanisco, L. Jaeglé, D. J. Jacob, E. J. Hints, E. J. Lanzendorf, J. G. Anderson, R. S. Gao, E. R. Keim, S. G. Donnelly, L. Del Negro, D. W. Fahey,

- S. A. McKeen, R. J. Salawitch, C. R. Webster, R. D. May, R. L. Herman, M. H. Proffitt, J. J. Margitan, E. L. Atlas, C. T. McElroy, J. C. Wilson, C. A. Brock, and T. V. Bui, "Hydrogen radicals, nitrogen radicals, and the production of ozone in the middle and upper troposphere," *Science* **279**, 49–53, 1998. The concentrations of the hydrogen radicals OH and HO<sub>2</sub> in the middle and upper troposphere were measured simultaneously with those of NO, O<sub>3</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub>, non-methane hydrocarbons, and with the ultraviolet and visible radiation field. The data allow a direct examination of the processes that produce O<sub>3</sub> in this region of the atmosphere. Comparison of the measured concentrations of OH and HO<sub>2</sub> with calculations based on their production from water vapor, ozone, and methane demonstrate that these sources are insufficient to explain the observed radical concentrations in the upper troposphere. The photolysis of carbonyl and peroxide compounds transported to this region from the lower troposphere may provide the source of HO<sub>x</sub> required to sustain the measured abundances of these radical species. The mechanism by which NO affects the production of O<sub>3</sub> is also illustrated by the measurements. In the upper tropospheric air masses sampled, the production rate for ozone (determined from the measured concentrations of HO<sub>2</sub> and NO) is calculated to be about 1 part per billion by volume each day. This production rate is faster than previously thought and implies that anthropogenic activities that add NO to the upper troposphere, such as biomass burning and aviation, will lead to production of more O<sub>3</sub> than expected.
4. Hints, E. J., P. A. Newman, H. H. Jonsson, C. R. Webster, R. D. May, R. L. Herman, L. R. Lait, M. R. Schoeberl, J. W. Elkins, P. R. Wamsley, G. S. Dutton, T. P. Bui, D. W. Kohn, and J. G. Anderson, "Dehydration and denitrification in the arctic polar vortex during the 1995–96 winter," *Geophys. Res. Lett.* **25**, 501–504 1998. Dehydration of more than 0.5 ppmv water was observed between 18 and 19 km ( $\theta \sim 450$ –465 K) at the edge of the arctic polar vortex on February 1, 1996. More than half the reactive nitrogen (NO<sub>y</sub>) had also been removed, with layers of enhanced NO<sub>y</sub> at lower altitudes. Back trajectory calculations show that air parcels sampled inside the vortex had experienced temperatures as low as 188 K within the previous 12 days, consistent with a small amount of dehydration. The depth of the dehydrated layer ( $\sim 1$  km) and the fact that trajectories passed through the region of ice saturation in one day imply selective growth of a small fraction of particles to sizes large enough ( $> 10$   $\mu$ m) to be irreversibly removed on this timescale. Over 25% of the arctic vortex in a 20–30 K range of  $\theta$  is estimated to have been dehydrated in this event.
  5. Hints, E. J., K. A. Boering, E. M. Weinstock, J. G. Anderson, B. L. Gary, L. Pfister, B. C. Daube, S. C. Wofsy, M. Loewenstein, J. R. Podolske, J. J. Margitan and T. P. Bui, "Troposphere-to-stratosphere transport in the lowermost stratosphere from measurements of H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O and O<sub>3</sub>," *Geophys. Res. Lett.* **25**, 2655–2658, 1998. The origin of air in the lowermost stratosphere is investigated with measurements from the NASA ER-2 aircraft. Air with high water vapor mixing ratios was observed in the stratosphere at  $\theta \sim 330$ –380 K near 40 N in May 1995, indicating the influence of intrusions of tropospheric air. Assuming that observed tracer-tracer relationships reflect mixing lines between tropospheric and stratospheric air masses, we calculate mixing ratios of H<sub>2</sub>O (12–24 ppmv) and CO<sub>2</sub> for the admixed tropospheric air at  $\theta = 352$ –364 K. Temperatures on the 355 K surface at 20–40 N

were low enough to dehydrate air to these values. While most ER-2 CO<sub>2</sub> data in both hemispheres are consistent with tropical or subtropical air entering the lowermost stratosphere, measurements from May 1995 for  $\theta < 362$  K suggest that entry of air from the midlatitude upper troposphere can occur in conjunction with mixing processes near the tropopause.

6. Stimpfle, R. M., R. C. Cohen, G. P. Bonne, P. B. Voss, K. K. Perkins, L. C. Koch, J. G. Anderson, R. J. Salawitch, S. A. Lloyd, R. S. Gao, L. A. Del Negro, E. R. Keim, and T. P. Bui, "The coupling of ClONO<sub>2</sub>, ClO and NO<sub>2</sub> in the lower stratosphere from *in situ* observations using the NASA ER-2 aircraft," *J. Geophys. Res.*, submitted December 1998. The first *in situ* measurements of ClONO<sub>2</sub> in the lower stratosphere, acquired using the NASA ER-2 aircraft during the Polar Ozone Loss in the Arctic Region in Summer (POLARIS) mission, are combined with simultaneous measurements of ClO, NO<sub>2</sub>, temperature, pressure, and the calculated photolysis rate coefficient ( $J_{\text{ClONO}_2}$ ) to examine the balance between production and loss of ClONO<sub>2</sub>. The observations demonstrate that the ClONO<sub>2</sub> photochemical steady state approximation,  $[\text{ClONO}_2]^{\text{PSS}} = k \times [\text{ClO}] \times [\text{NO}_2] / J_{\text{ClONO}_2}$ , is in good agreement with the direct measurement,  $[\text{ClONO}_2]^{\text{MEAS}}$ . For the bulk of the data (80%), where  $T > 220$  K and latitudes  $> 45^\circ\text{N}$ ,  $[\text{ClONO}_2]^{\text{PSS}} = 1.15 \pm 0.36 (1\sigma) \times [\text{ClONO}_2]^{\text{MEAS}}$ , while for  $T < 220$  K and latitudes  $< 45^\circ\text{N}$  the result is somewhat less at  $1.01 \pm 0.30$ . The cause of the temperature and/or latitude trend is unidentified. These results are independent of solar zenith angle and air density, thus there is no evidence in support of a pressure-dependent quantum yield for photodissociation of ClONO<sub>2</sub> at wavelengths  $> 300$  nm. These measurements confirm the mechanism by which active nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) controls the abundance of active chlorine ( $\text{Cl}_x = \text{ClO} + \text{Cl}$ ) in the stratosphere.

The field deployment grant was extended, subsequently, to include the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS). That mission was flown between April 1997 and October 1997. Abstracts are presented for the following papers, which have been submitted for publication in a special issue of *Journal of Geophysical Research—Atmospheres*, scheduled for publication in Fall 1999:

1. Lazendorf, E. J., T. F. Hanisco, R. M. Stimpfle, J. G. Anderson, P. O. Wennberg, R. L. Herman, R. C. Cohen, D. W. Fahey, R. S. Gao, C. R. Webster, R. D. May, J. J. Margitan, and T. P. Bui, "Establishing the dependence of  $[\text{HO}_2]$  on temperature, halogen loading, ozone, and NO<sub>x</sub>," *J. Geophys. Res.*, submitted 1999. A large database of measurements from the last three NASA ER-2 field campaigns is used to examine HO<sub>x</sub> (HO + HO<sub>2</sub>) photochemistry in the lower stratosphere and upper troposphere. These measurements cover a latitude range of 70°S to 90°N and a wide variety of atmospheric conditions. *In situ* measurements of the chemical species important in HO<sub>x</sub> partitioning are compared to laboratory-measured reaction rates by examining the ratio of HO<sub>2</sub>/OH. HO<sub>x</sub> partitioning is accurately described ( $\pm 10\%$ ) by mechanisms that include the rate limiting steps for (1) direct and indirect removal of O<sub>3</sub> by HO<sub>x</sub> in the lower stratosphere, and (2) the production of O<sub>3</sub> in the upper troposphere. Because [OH] is roughly constant in the lower stratosphere, the ratio of HO<sub>2</sub>/OH reflects the variability of [HO<sub>2</sub>] to the concentrations of other chemical species. The response of the HO<sub>2</sub>/OH ratio shows how HO<sub>x</sub> concentrations respond to

- photochemical changes. The effects of halogen loading,  $[O_3]$ ,  $[NO_x]$ , and temperature, upon the  $HO_2/OH$  ratio are examine.
2. Perkins, K. K., T. F. Hanisco, R. C. Cohen, L. C. Koch, R. M. Stimpfle, P. B. Voss, G. P. Bonne, E. J. Lanzendorf, J. G. Anderson, P. O. Wennberg, R. -S. Gao, L. A. Del Negro, E. R. Keim, S. G. Donnelly, D. W. Fahey, and R. J. Salawitch, "An examination of the  $NO_2/HNO_3$  ratio in the lower stratosphere during periods of continuous sunlight," *J. Geophys. Res.*, submitted 1999. During the 1997 Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission, simultaneous, *in situ* observations of the principal radical and reservoir species of the nitrogen, hydrogen, and halogen families were obtained in the high-latitude, lower stratosphere during summer. These observations are ideal for examining the steady-state partitioning between  $NO_2$  and  $HNO_3$  during periods of continuous sunlight where the exchange between  $NO_2$  and  $HONO_3$  is dominated by gas-phase processes. Calculations of  $NO_x$  production and loss show that when 1997 JPL rate coefficient recommendations are used, loss exceeds production by 53%, where a balance is expected. Using new laboratory measurements of the reaction rate coefficients for  $OH + HNO_3$  and  $OH + NO_2$  reduces this discrepancy to 11%. Combining this analysis with an analogous, but independent, analysis of the  $HO_x$  system indicates that the precision in estimating overhead  $O_3$  from TOMS satellite measurements is sufficiently poor as to hamper analyses of both systems. The measurements also exhibit a strong, almost linear correlation between the photolysis rate of  $HNO_3$  ( $J_{HNO_3}$ ) and  $[OH]$ , which results in a remarkably constant partitioning between the two  $NO_x$  production processes with  $HNO_3$  photolysis and reaction with  $OH$ , accounting for 59% and 41% of the production, respectively. Because of strong  $J_{HNO_3}$ - $OH$  relationship, the steady-state  $[NO_2]_{24hr-avg}/[HNO_3]$  ratio reduces to a simple function of temperature and  $[M]$ . Indeed, the *in situ* observations reveal a compact relationship between the  $[NO_2]_{24hr-avg}/[HNO_3]$  ratio and  $[M]$  over a range of latitude,  $[O_3]$ ,  $[NO_y]$ , particle surface area, albedo, and overhead  $O_3$ . Because of the simplicity of this functional relationship, the steady-state  $[NO_2]_{24hr-avg}/[HNO_3]$  ratio can be easily and accurately predicted throughout the region of continuous sunlight.
  3. Hanisco, T. F., E. J. Lanzendorf, R. M. Stimpfle, G. P. Bonne, E. J. Hintsa, K. K. Perkins, R. M. Stimpfle, P. B. Voss, J. G. Anderson, P. O. Wennberg, R. Herman, R. C. Cohen, L. C. Koch, D. W. Fahey, R. -S. Gao, E. R. Keim, S. G. Donnelly, L. A. Del Negro, M. H. Proffitt, R. J. Salawitch, C. R. Webster, R. D. May, S. A. Lloyd, T. McElroy, C. Midwinter, and P. Bui, "Sources, sinks, and the distribution of  $OH$  in the lower stratosphere," *J. Geophys. Res.*, submitted 1999. Extensive measurement campaigns by the NASA ER-2 have obtained a pole-to-pole database of the species that control  $HO_x$  ( $OH + HO_2$ ) chemistry. The wide dynamic range of these *in situ* measurements provides an opportunity to gain insight into the mechanisms that control the  $HO_x$  system. Measurements in the lower stratosphere show a remarkably tight correlation of  $OH$  concentration with Solar Zenith Angle (SZA), which is invariant over latitudes ranging from  $70^\circ S$  to  $90^\circ N$  and all seasons. Calculations using *in situ* measurements show that the production rate of  $OH$  is proportional to  $O_3$  and ultraviolet radiation flux and the loss rate is proportional to the concentration of  $NO_y$  (reactive nitrogen). Since  $O_3$  and  $NO_y$  are correlated, the concentration of  $OH$  is fairly

constant within this data set. Changes in the partitioning within  $\text{NO}_y$  have a dramatic effect on the loss rates of  $\text{HO}_x$ , but little or no impact on the measured abundance of OH. The heterogeneous conversion of  $\text{NO}_2$  to  $\text{HNO}_3$  is not a net source of  $\text{HO}_x$  because production and removal cycles are nearly balanced. Furthermore, the enhanced loss rates at high  $\text{NO}_2/\text{HNO}_3$  are offset by increased photolysis rates resulting from decreased  $\text{O}_3$  column above the ER-2.

4. Bonne, G. P., R. M. Stimpfle, R. C. Cohen, P. B. Voss, K. K. Perkins, J. G. Anderson, C. R. Webster, D. C. Scott, R. D. May, R. J. Salawitch, J. W. Elkins, R. E. Dunn, G. S. Dutton, K. W. Jucks, G. C. Toon, and B. Sen, "An examination of the inorganic chlorine budget in the lower stratosphere," *J. Geophys. Res.*, submitted 1999. We use the first simultaneous *in situ* measurements of  $\text{ClONO}_2$ ,  $\text{ClO}$ , and  $\text{HCl}$  acquired using the NASA ER-2 aircraft during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission to test whether these three compounds quantitatively account for total inorganic chlorine ( $\text{Cl}_y$ ) in the lower stratosphere in 1997. We find  $(\text{ClO} + \text{ClONO}_2 + \text{HCl})/\text{Cl}_y = 0.92 \pm 0.10$ , where  $\text{Cl}_y$  is inferred from *in situ* measurements of organic chlorine source gases. These observations are consistent with our current understanding of the budget and partitioning of  $\text{Cl}_y$  in the lower stratosphere. We find no evidence in support of missing inorganic chlorine species that comprise a significant fraction of  $\text{Cl}_y$ . We apply the analysis to earlier ER-2 observations dating from 1991 to investigate possible causes of previously observed discrepancies in the inorganic chlorine budget. Using space shuttle, satellite, balloon and aircraft measurements in combination with ER-2 data we find that the discrepancy is unlikely to have been caused by missing chlorine species or an error in the photolysis rate of chlorine nitrate. We also find  $\text{HCl}/\text{Cl}_y$  is not significantly controlled solely by aerosol surface area density in the lower stratosphere.
5. Bonne, G. P., R. M. Stimpfle, R. C. Cohen, P. B. Voss, K. K. Perkins, L. C. Koch, E. J. Hints, S. A. Lloyd, and J. G. Anderson, "*In situ* measurements of  $\text{ClONO}_2$ : A new thermal dissociation resonance fluorescence instrument on board the NASA ER-2 aircraft," *J. Geophys. Res.*, submitted 1999. A new instrument for the *in situ* measurement of  $\text{ClONO}_2$  density in the lower stratosphere from the NASA ER-2 aircraft is described. The technique of thermal dissociation of  $\text{ClONO}_2$  is coupled with the proven chemical conversion/atomic resonance scattering technique for measurement of  $\text{ClO}$ . The sampled ambient air stream is heated to 520 K, thermally dissociating  $\text{ClONO}_2$  to  $\text{ClO}$  and  $\text{NO}_2$  within 5 msec. The  $\text{ClO}$  fragment is reacted with added  $\text{NO}$  to form  $\text{Cl}$  atoms, which are detected using atomic resonance fluorescence at 118.9 nm. Laboratory calibrations and aircraft measurements demonstrate that the technique can be described by gas phase processes.  $\text{ClONO}_2$  is detected with an accuracy of 20% ( $1 \sigma$ ) and a detection threshold of 10 parts per trillion in a 35-second integration time. The instrument has provided the first *in situ* measurements of  $\text{ClONO}_2$  during the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission staged out of Fairbanks, AK in 1997. These measurements, taken with other simultaneous measurements from the ER-2, provide the means for a detailed examination of the budget and partitioning of inorganic chlorine and the production and loss of  $\text{ClONO}_2$  in the lower stratosphere.

6. Voss, P. B., R. M. Stimpfle, T. F. Hanisco, G. P. Bonne, K. K. Perkins, E. J. Lanzendorf, J. G. Anderson, R. C. Cohen, L. C. Koch, C. R. Webster, D. C. Scott, R. D. May, R. J. Salawitch, J. J. Margitan, P. O. Wennberg, R. -S. Gao, T. P. Bui, P. A. Newman, and L. R. Lait, "Chlorine partitioning in the summer lower stratosphere: A comparison of modeled and measured chlorine partitioning during POLARIS," *J. Geophys. Res.*, submitted 1999. The first *in situ* measurements of ClONO<sub>2</sub> (made during the POLARIS campaign in the summer of 1997) are used in conjunction with calculated photolysis rates and measurements of HCl, O<sub>3</sub>, CH<sub>4</sub>, NO, NO<sub>2</sub>, and OH to examine the processes that control gas-phase partitioning of Cl<sub>y</sub> in the lower stratosphere. Diurnal steady-state and trajectory models of gas-phase chlorine chemistry (constrained by measured OH and NO<sub>x</sub>) demonstrate that the rate constants and photolysis cross-sections of JPL97 overpredict [ClONO<sub>2</sub>]/[HCl] by 45–60% in comparison with measurements. This error is significantly greater than reported in previous studies that mask errors in Cl<sub>y</sub> partitioning by using modeled OH. A treatment of ratio statistics quantifies model-measurement dispersion; for the ratio [ClONO<sub>2</sub>]/[HCl], dispersion is reduced significantly when photolysis rates are based on average climatology instead of local conditions. A framework for this analysis is provided by averaging a steady-state approximation for [ClONO<sub>2</sub>]/[HCl] and factoring it into chemical, photolytic, and meteorological terms. This separation elucidates the effects of latitude, season, and altitude on Cl<sub>y</sub> partitioning. A method for estimating time constants is developed and used to demonstrate that [ClONO<sub>2</sub>]/[HCl] reaches steady-state with an *e*-folding time of approximately 2–10 days.
7. Smith, J. B., E. J. Hints, and J. G. Anderson, "Mechanisms for midlatitude ozone loss: Cirrus clouds in the stratosphere?" *J. Geophys. Res.*, submitted 1999. The question of midlatitude ozone erosion by chlorine free radical catalytic destruction is examined. Simultaneous, high-resolution observations of ClO, H<sub>2</sub>O, tropopause position, particle reactive surface area, and ice saturation occurrence frequency obtained from the NASA ER-2 are presented. The objective is to test the hypothesis that the existence of cirrus clouds or cold aerosols in the first few kilometers above the tropopause at midlatitudes is responsible for increasing the ratio of chlorine free radicals to total inorganic chlorine and thus amplifying the rate of catalytic ozone destruction. The observations reveal a sharp decrease in cloud occurrence frequency immediately above the tropopause, a marked degree of undersaturation immediately above the tropopause, a corresponding sharp gradient in the product of cold aerosol reactive surface area and reaction probability,  $\gamma S_a$ , and, finally, the consistent absence of enhanced concentrations of ClO immediately above the tropopause. These results suggest that midlatitude ozone erosion is not controlled *in situ* by the mechanism of cirrus cloud and/or cold aerosol enhancement of chlorine radicals in the vicinity of the tropopause.